

Тема 19БФ037-02

ПРОЕКТ:

Фундаментальні засади створення наногібридних функціональних композитів, синтезованих в полімерних матрицях, здатних реагувати на зовнішні фактор

(Науковий керівник: д. х. н. Н.В. Куцевол)

PROJECT:

Fundamental principles of the creation of nanohybrid functional composites synthesized in polymer matrices capable to react to external stimuli



Branched polymers, pH and thermosensitive nanosystems for biomedical application

Group leader: Dr. Sci. Kutsevol N.

Collaborations:

- Institute Charles Sadron, Strasbourg, France
- Kavetsky Institute of Experimental Pathology, Oncology and Radiobiology, NASU
- Belarussian State University
- Iv.-Frankivsk National Medical University
- B.I. Verkin Institute for Low Temperature Physics and Engineering, NASU
- ISMA NASU
- Bogomoletz Institute of Physiology

Photosensitive polymers and nanocomposites for photonics application

Group leader: PhD Krupka O.

Collaborations:

- Angers University, Laboratory MOLTECH-Anjou, UMR CNRS 6200, Angers, France
- Institute of Physics, Nicholas Copernicus University, Torun, Poland
- Faculty of Chemistry, Wroclaw University of Science and Technology, Wroclaw, Poland
- Department of Solid State Physics, Faculty of Physics, Ivan Franko National University of L'viv, L'viv, Ukraine

Branched polymers, pH and thermosensitive nanosystems for biomedical application

Group leader : Dr. Chem. Sci. Nataliya Kutsevol

The team:

Chemists:

PhD V. Chumachenko

PhD student Yu. Harahuts

PhD O. Nadтока

PhD O. Boyko

Physicists:

PhD A. Naumenko

Dr.Sci. O.Yeshchenko

Biologist:

PhD P.Virychn

We are focused on fundamental aspects of synthesis and characterization of branched uncharged polymers and polyelectrolytes in solution as well as stimuli responsible branched polymers and nanosystems synthesized in situ into these polymer matrices. We study the response of these complicated systems towards external stimuli (pH, T ...) and their applications mainly in biomaterials or drug delivery fields.

Branched polymer matrices have various chemical nature and internal structure, higher local concentration of functional groups in comparison with their linear analogue, and they can be very efficient for designing of optimized nanocarriers-nanosystems for medical applications and for water treatment. We are working in collaboration with physicists and biologists.

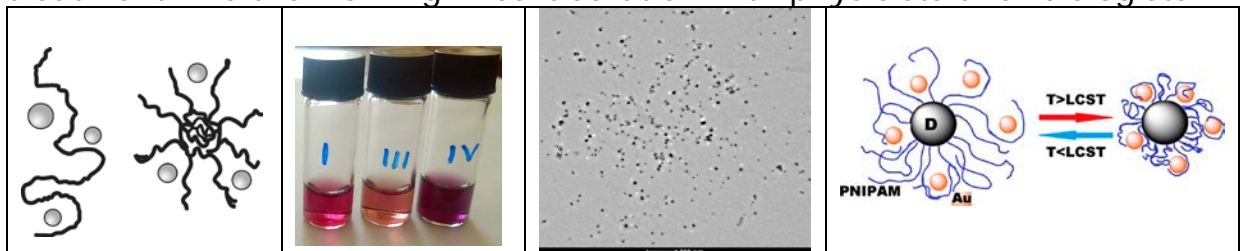
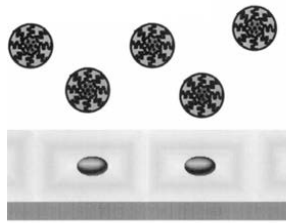


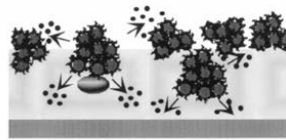
Figure 1. Nanosystems, synthesized into stimuli responsible polymer matrices of various architecture and internal structure.

polymeric micelle-drug complex



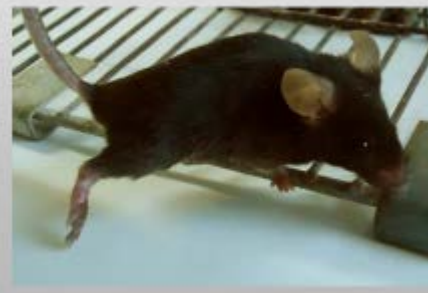
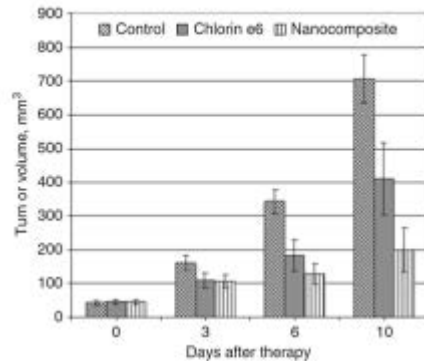
below LCST

drug release acceleration and cellular adsorption enhancement



above LCST

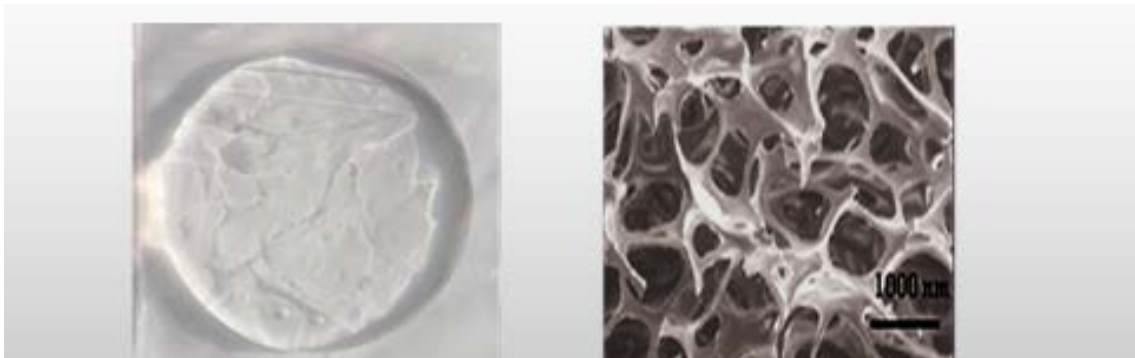
Temperature and pH-modulated drug release with polymer nanocarrier and enhanced cellular adsorption with polymer nanosystems.



Photodynamic therapy of Lewis lung carcinoma using chlorin e6 or its nanocomposite, based on D-g-PAA(PE) polymer matrix

V. A. Chumachenko, I. O. Shton, E. D. Shishko, N. V. Kutsevol, A. I. Marinin and N. F. Gamaleia, Chapter in the Book: Nanophysics, Nanophotonics, Surface Studies, and Applications, 2016, V, 183, Springer Proceedings in Physics, pp 379-390

Hydrogels for biomedical applications (PhD Nadtoka O)



Methodological and Technical Expertise

1. Chemical modeling of branched polymers
2. Synthesis of nanosystems into polymer matrices
3. All experimental approaches for characterization of polymers of complicated internal structure and nanosystems: elastic and quasy elastic light scattering, chromatography, transmission electron microscopy, differential scanning calorimetry, viscometry, potentiometric titration etc.

Selected publications

1. Kutsevol N., Bezugla T., Bezuglyi M., Rawiso M. Branched Dextran-Graft-Polyacrylamide Copolymers as Perspective Materials for Nanotechnology. *Macromol. Symp.* 2012. -V.317-318, Iss. 1.- P.82-90.
2. N. Kutsevol, M. Bezuglyi, M. Rawiso, T. Bezugla. Star-like Dextran-graft-(polyacrylamide-co-polyacrylic acid) Copolymers. *Macromol. Symp.* 2014, 335, P.12-16.
3. N.V.Kutsevol, T.N. Bezuglaya, N. Yu. Bezuglyi. Features of the intramolecular structure of branched polymer systems in solution. *Journal of Structural Chemistry.* 2014. V.55, №3, P.575-587.
4. V. Chumachenko, N. Kutsevol, M. Rawiso, M. Schmutz, C. Blanck. In situ formation of silver nanoparticles in linear and branched polyelectrolyte matrices using various reducing agent. *Nanoscale Research Letters.* 2014, 9: 164.
5. N.V. Kutsevol, V.A. Chumachenko, M. Rawiso, V.F. Shkodich, O.V. Stoyanov. Star-like polymers dextran-polyacrylamide: the prospects of application for nanotechnology. *Journal of Structural Chemistry.* 2015.V.56, №5. P.1016-1023.
6. Leonid Bulavin, Nataliya Kutsevol, Vasyl Chumachenko, Dmytro Soloviov, Alexander Kuklin, Andriy Marinin. SAXS combined with UV-vis spectroscopy and QUELS: accurate characterization of silver sols synthesized in polymer matrices. *Nanoscale Research Letters.* 2016. 11:35.
7. Yeshchenko, O.A., Kutsevol, N.V., Naumenko, A.P. Light-Induced Heating of Gold Nanoparticles in Colloidal Solution: Dependence on Detuning from Surface Plasmon Resonance 2016. *Plasmonics.* 11 (1). P. 345–350.
8. N. Kutsevol, V. Chumachenko, M. Rawiso, A. Shyichuk. Green synthesis of silver nanoparticles using glucose as reducing agent and dextran-graft-polyacrylamide as template. *Micro & Nano letters,* 2016, V.11, Issue 5, P. 256-259.
9. V. A. Chumachenko, A. P. Naumenko, O. A. Yeshchenko, N.V. Kutsevol, I.S. Bondarchuk Synthesis, morphology and optical properties of Au/Cds hybride nanocomposites stabilized by branched polymer matrices. *Journal of Nanomaterials.* 2016. Volume 2016. Article number 1439437.
10. P. Telegeeva, N. Kutsevol, S. Filipchenko, G. Telegeev. Dextran-Polyacrylamide as Nanocarrier for Targeted Delivery of Anticancer Drugs into Tumor Cells. In Book "Chemical Engineering of Polymers Production of Functional and Flexible Materials", Eds. O.V. Mukbaniany, M.J. Abadie, T. Tatrishvili. Part 2, Chapter 15. 396 p.
11. V. A. Chumachenko, I. O. Shton, E. D. Shishko, N. V. Kutsevol, A. I. Marinin and N. F. Gamaleia. Branched Copolymers Dextran-Graft-Polyacrylamide as Nanocarriers for Delivery of Gold Nanoparticles and Photosensitizers to Tumor Cells. Chapter in the Book: *Nanophysics, Nanophotonics, Surface Studies, and Applications,* 2016. Volume 183 of the series *Springer Proceedings in Physics/* pp 379-390. Eds: Olena Fesenko, Leonid Yatsenko
12. A. Naumenko, N. Kutsevol, V. Chumachenko, V. Pashchenko, S. Kutovyy, M. Rawiso. Synthesis and characterization of CdS nanoparticles obtained in star-like Dextran-graft-Polyacrylamide matrices *Ukrainian Journal of Physics.* 2017. Vol. 62, No. 10 . P. 908-912. (Scopus)
13. V. Chumachenko, N. Kutsevol, Yu. Harahuts, M. Rawiso, A. Marinin, L. Bulavin. Star-like Dextran-graft-PNiPAM copolymers. Effect of internal molecular structure on the phase transition. *Journal of Molecular Liquids.* 2017. V.235, P.77-82.
14. Kutsevol, N., Naumenko, A., Chumachenko, V., Balega, A., Bulavin, L. Flocculative ability of uncharged and hydrolyzed graft and linear polyacrylamides. *Journal of Molecular Liquids.* 2017. 227, P. 26-30.
15. G. Telegeev, N. Kutsevol, V. Chumachenko, A. Naumenko, P. Telegeeva, S. Filipchenko, and Yu. Harahuts. Dextran-Polyacrylamide as Matrices for Creation of Anticancer Nanocomposite. *International Journal of Polymer Science.* 2017. Article ID 4929857.

16. N. Kutsevol, V. Chumachenko, Yu. Harahuts, A. Marinin. Aging process of gold nanoparticles synthesized in situ in aqueous solutions of polyacrylamides. In Book "Chemical Engineering of Polymers. Production of Functional and Flexible Materials", Eds. O.V. Mukbanianym M.J. Abadie, T. Tatrishvili. Part 2, Chapter 10. pp.119-129 p., 2017.
17. P. Telegeeva, N. Kutsevol, S. Filipchenko, G. Telegeev. Dextran-Polyacrylamide as Nanocarrier for Targeted Delivery of Anticancer Drugs into Tumor Cells. In Book "Chemical Engineering of Polymers Production of Functional and Flexible Materials", Ed. O.V. Mukbaniany, M.J. Abadie, T. Tatrishvili. Part 2, Chapter 15. Pp.183-195 p.
18. Georgiy Smolyakov, Jean-Marie Catala, Nataliya Kutsevol, Michel Rawiso. Influence of the Nature of Counterions and Solvent on PSS Structure in Solutions, Modern Problems of Molecular Physics, Springer Proceedings in Physics 197, L. A. Bulavin and A. V. Chalyi (eds.). Chapter 7. P. 133-147.
19. Yeshchenko, O.A., Kozachenko, V.V., Naumenko, A.P., Berezovskaa, N.I., Nataliya V. Kutsevol, N.V., Chumachenko, V.A., Haftel, M., Pinchuk, A.O. Gold nanoparticle plasmon resonance in near-field coupled Au NPs layer/Al film nanostructure: Dependence on metal film thickness. *Photonics and Nanostructures - Fundamentals and Applications*. 2018. 29. P. 1–7.
20. Anna Grebinyk, Valeriy Yashchuk, Nataliya Bashmakova, Dmytro Gryn, Tobias Hagemann, Antonina Naumenko, Nataliya Kutsevol, Thomas Dandekar, Marcus Frohme. A new triple system DNA-Nanosilver-Berberine for cancer therapy. *Applied Nanoscience*. 2018. <https://doi.org/10.1007/s13204-018-0688-x>
21. N. Kutsevol, A. Naumenko, Yu. Harahuts, V. Chumachenko, I. Shton, E. Shishko, N. Lukianova, V. Chekhun. New hybrid composites for photodynamic therapy: synthesis, characterization and biological study. *Appl Nanosci* (2018). P.1-8. <https://doi.org/10.1007/s13204-018-0768-y>
22. Oleg A. Yeshchenko, Antonina P. Naumenko, Nataliya V. Kutsevol, Daria O. Maskova, Iulia I. Harahuts, Vasyl A. Chumachenko, Andrey I. Marinin. Anomalous Inverse Hysteresis of Phase Transition in Thermosensitive Dextran-graft-PNIPAM Copolymer/Au Nanoparticles Hybrid Nanosystem. *J. Phys. Chem. C*, 2018, 122 (14), pp 8003–8010.
23. M. Yu. Losytskyy, L. O. Vretik, N. V. Kutsevol, O. A. Nikolaeva and V. M. Yashchuk. *I. Nanoscale Research Letters* (2018) 13:166
24. Kutsevol, N., Naumenko, A., Chumachenko, V., Yeshchenko, O., Harahuts, Y., Pavlenko, V. Aggregation processes in hybrid nanosystem polymer/nanosilver/cisplatin. *Ukrainian Journal of Physics*. Volume 63, Issue 6, 12 July 2018, Pages 513-520.
25. Nadtoka O., Kutsevol N., Onanko A., Neimash V. (2018) Mechanical and Thermal Characteristics of Irradiation Cross-linked Hydrogels. In: Fesenko O., Yatsenko L. (eds) *Nanochemistry, Biotechnology, Nanomaterials, and Their Applications*. NANO 2017. Springer Proceedings in Physics, vol 214. Springer, Cham. P.205-214.
26. O. Nadtoka & N. Kutsevol. Thermal analysis of cross-linked hydrogels based on PVA and D-g-PAA obtained by various methods. *Molecular Crystals and Liquid Crystals*, Volume 661, 2018 - Issue 1. P.52-57.
27. N. Kutsevol, A. Glamazda, Chumachenko, Yu. Harahuts, S. G. Stepanian, A. M. Plokhotnichenko, V. A. Karachevtsev. Behavior of hybrid thermosensitive nanosystem dextran-graft-pnipam/gold nanoparticles: characterization within LCTS. *Journal of Nanoparticle Research*. 2018. *J Nanopart Res* (2018) 20: 236.
28. Tatiana Matvienko, Viktoriya Sokolova, Svitlana Prylutska, Yuliia Harahuts, Nataliya Kutsevol, Viktor Kostjukov, Maxim Evstigneev, Yuriy Prylutsky, Matthias Epple, Uwe Ritter. In vitro study of the anticancer activity of various Doxorubicin-containing dispersions. *Bioimpacts*. 2019; 9(1):59-70.
29. M.Y. Losytskyy, R.A. Kharchenko, Y.I. Harahuts, E.A. Shirinyan, Y.V. Malinovska, N.V. Kutsevol, V.M. Yashchuk. Different effect of polymer-incorporated nanoparticles of Au and Ag on hematoporphyrin interaction with graft polymers. *Funct. Mater.* 2019; 26 (1): 107-113.

Photosensitive polymers and nanocomposites for photonics application

Group leader : PhD Oksana Krupka

The team:

**PhD Vitaliy Smokal,
PhD Oksana Kharchenko**

Our group is interested in synthesis and characterization of photoactive polymers and nanocomposites. Our activities are on new photo switchable polymer materials with chromophore in side chain; developing new polymer systems with different structures of photoactive fragments and nanocomposites for optical application.

Photochemical properties of such polymers can be advantageous addressed for photonics and nonlinear optics. In addition, the spatial organization of the active side chain residues along the polymeric backbone is of critical importance regarding mechanical and structural properties of the material. This allows by an optical control to give rise to encoded images at the nanoscale. In the other hand the possibility of a continuous tuning of the optical and electronic properties by varying the size of the particles in nanocomposite, such materials can be viewed as promising candidates for future applications in the field of sensor technology, transistor, electrode materials, logic circuits and laser working.

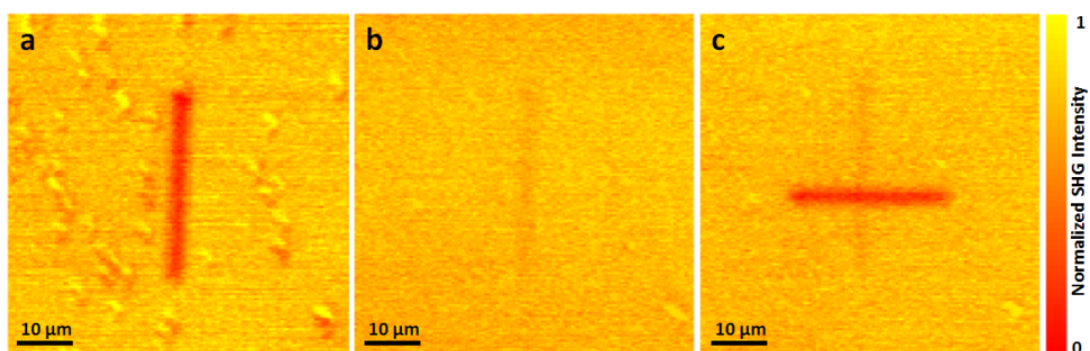
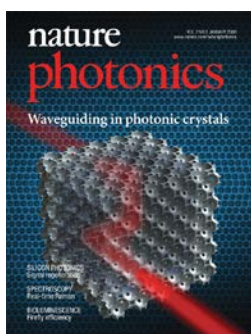


Fig 1. SHG image after recording (a)- erasing (b)- writing (c) on the coumarin-polymer film.

New method of optical storage based on the reversible photo switchable process of side chain polymer films, enables highly efficient optical data storage, opening promising perspectives in the important and sensitive field

of hidden 3D data storage, (in collaboration with Angers University, Laboratory MOLTECH-Anjou, UMR CNRS 6200, Angers).



We have shown the potentiality of modified DNA for holographic recordings « Nature Photonics », Research Highlights, DNA stripes, 2, 6-7, (2008) Impact Factor: 34,16

Methodological and Technical Expertise

- Chemical modeling of polymers
- All experimental approaches for characterization of polymers: self-exclusion chromatography, thermogravimetric analysis, differential scanning calorimetry, atom-force microscopy etc.
- Some experimental approaches for nonlinear optical effects in organic compounds/organic polymers (dye-doped polymers, molecules); optical data storage; optical properties of nanostructured materials/nanocomposites

Selected publications

1. V. Smokal, O. Krupka, B. Derkowska-Zielinska, K. Matczyszyn, M Dudek, M. Samoc, R. Czaplicki, A. Kaczmarek-Kedziera, A. Biitseva, All-Optical Poling and Two-Photon Absorption in Heterocyclic Azo Dyes with Different Side Groups, *J. Phys. Chem. C*, 123 (1), 2019, pp 725–734. (IF 4.484)
2. V. Smokal, O. Kharchenko, O. Krupka, D. Guichaoua, B. Kulyk, A. Migalska-Zalas, O. Kolendo, B. Sahraoui: UV Irradiation Induce NLO Modulation in Photochromic Styrylquinoline-based Polymers: Computational and Experimental Studies, *Org. Electron*, 66, 2019, pp. 175-182. (IF 3.68)
3. V. Smokal, O. Krupka, D. Trefon-Radziejewska, G. Hamaoui, M. Chirtoc, N. Horny, A. Biitseva, B. Derkowska-Zielinska Thermophysical properties of methacrylic polymer films with guest-host and side-chain azobenzene, *Materials Chemistry and Physics*, 223, 2019, 700-707. (IF 2.21)
4. V.Smokal, O.Kharchenko, O.Krupka, B.Derkowska-Zielinska, L.Skowronski, M.Sypniewska, D.Chomickia, M.Naparty, Functionalized polymers with strong push-pull azo chromophores in side chain for optical application, *Optical Materials*, 85, 2018, 391-398. (IF 2.320)
5. Krupka, V. Smokal, B. Kulyk, V. Figà, R. Czaplicki, B. Sahraoui, Nonlinear optical behavior of DNA-functionalized gold nanoparticles, *Applied Nanoscience*, 2018, 1-6.

(Applied Nanoscience IF 2.95)

6. Smokal, V., Krupka, O., Derkowska-Zielinska, B., Skowronski, L., Blitseva, A., Grabowski, A., Naparty, M.K., Kysil, A., Optical characterization of new heterocyclic azo dyes containing polymers thin films, *Applied Surface Science*, 427, 2017, 361-366. (IF 4.439; WS 04/2019: 7 citations)
7. B. Kulyk, V. Kapustianyuk, V. Tsybulskyy, O. Krupka, B. Sahraoui, Optical properties of ZnO/PMMA nanocomposite films. *Journal of Alloys and Compounds*, 502, (1), 2010, 24-27. (IF 3.779; WS 04/2019: 59 citations)
8. K. Iliopoulos, O. Krupka, D. Gindre, M. Sallé, Reversible Two-Photon Optical Data Storage in Coumarin-Based Copolymers *J. Am. Chem. Soc.*, 132 (41), (2010), 14343–14345. (IF 14.357; WS 04/2019: 69 citations)
9. R. Czaplicki, O. Krupka, Z. Essaidi, El-Ghayoury, J.G. Grote, F. Kajzar, B. Sahraoui, Grating inscription in picosecond regime in thin films of functionalized DNA, *Optic Express*, 15, (2007), 15268-15273 (IF 3.356; WS 04/2019: 66 citations)
10. Krupka, A. El-Ghayoury, I. Rau, B. Sahraoui, J.G. Grote, F. Kajzar, NLO properties of functionalized DNA thin film, *Thin Solid Films*, 516, (2008), 8932–8936 (IF 1.939; WS 04/2019: 55 citations)